SYNTHESIS OF MESOPOROUS MOLECULAR SIEVES AND THEIR APPLICATION FOR CATALYTIC CONVERSION OF POLYCYCLIC AROMATIC HYDROCARBONS

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INTRODUCTION

Molecular sieves such as Y and ZSM-5 are widely used catalysts in acid-catalyzed reactions for the production of fuels, petrochemicals, and fine chemicals [1-3]. Despite their enormous use as environmentally safe catalysts, they are limited to convert relatively small molecules as their pore size is restricted to micropore size range (usually 1.4 nm). However, with the growing demand of technologies for treating heavier feeds, as well as for synthesizing large molecules for producing commodities and fine chemicals, it is necessary to develop catalysts with wider pores. Recently, Mobil workers have reported a new series of mesoporous molecular sieves [4,5]: MCM-41 is one of the members of this extensive family of mesoporous series possessing a hexagonal array of uniform mesopores. Many reports have since appeared on synthesis and characterization of these new materials [6-10]. However, information on their catalytic activity is still very limited. The pore dimensions of these materials can be tailored (in the range of 1.5-10.0 nm or more) through the choice of surfactant and auxiliary chemicals as templates and the crystallization conditions in the synthesis procedure. The BET surface area of these materials is more than 1000 m^2/g with high sorption capacities of 0.7 cc/g and greater. Moreover, these materials can be synthesized in a large range of framework Si/Al ratios and therefore can develop acid sites of different strength. Hence, these new mesoporous aluminosilicate molecular sieves, Al-MCM-41, might open new possibilities in developing catalysts for processing large molecules.

As part of our ongoing project on liquefaction of coal and upgrading of coal liquids, we intend to use these mesoporous aluminosilicates molecular sieves as catalysts to upgrade the coal derived oils to transportation fuels, particularly thermally stable jet fuels. We have studied the synthesis and characterization of these materials [11]. In this paper, we report some of the results on the synthesis and their application for the catalytic conversion of model polycyclic aromatic hydrocarbon compounds.

EXPERIMENTAL

The mesoporous aluminosilicate molecular sieves, Al-MCM-41, were synthesized hydrothermally in 100 ml Teflon lined autoclaves from a mixture of reactants with the following composition: $50SiO_2$-xAl_2O_3-$2.19(TMA)_2O$-$15.62(CTMA)Br$-$3165H_2O$; where x=0.5, 1.0 and 2.0. The details of synthesis are given elsewhere [11]. Three series of samples with varying Si/Al ratios, and using three different aluminum sources (aluminum isopropoxide, pseudo boehmite and aluminum sulfate) were synthesized. Some synthesis parameters and their physical characteristics are shown in Table 1. The Al-MCM-41 samples were characterized by chemical analysis, X-ray diffraction, nitrogen adsorption, thermogravimetric analysis, and solid state NMR.

Prior to catalytic runs, the organic template from the as-synthesized solids was removed by calcining the samples in a tubular furnace at 550 °C for one hour in nitrogen and 6 hours in air flow. The calcined samples were exchanged with ammonium nitrate. The protonated form was then obtained by calcining these ammonium exchanged samples at 550 °C for 3 hours. Finally, 3wt% Pt was loaded by wet impregnation, with a required amount of hexachloro platonic acid (Aldrich) solution and the sample in a beaker and evaporating the water at room temperature while stirring it overnight. The Pt loaded samples were then calcined in air at 450 °C for 3 hours.

Mesoporous molecular sieve catalysts were tested for the following reactions: 1) hydrogenation of naphthalene and phenanthrene, 2) isopropylation of naphthalene and 3) hydrocracking of 1,3,5-triisopropyl benzene. A 30 cc stainless-steel tubing bomb batch reactor was used for all the experiments. During the reaction, reactors were heated in a fluidized sand-bath under vertical shaking (240 cycles/min.). All the chemicals were used as supplied. The standard reactor charge was 0.10 g of catalyst and 1.0 g of reactant and other reaction conditions are given in appropriate Tables. At the end of the reaction, the reactor was quenched in cold water. After collecting the reaction products in acetone solution, they were analyzed by GC (Perkin-Elmer 8500) using DB-17 fused silica capillary column. The products were identified by GC-MS (HP).

RESULTS AND DISCUSSIONS

Three series of Al-MCM-41 samples using three different aluminum sources, aluminum isopropoxide, pseudo boehmite (Catapal B), and aluminum sulfate, with Si/Al ratios 50, 25, and 12.5 were synthesized. Details are shown in Table 1. The crystallinity, the incorporation of aluminum in framework and the acidity were studied by XRD, nitrogen sorption, thermal analysis of n-butylamine on samples, ^{27}Al MAS NMR. The results on the synthesis and characterization were reported in our earlier paper [11]. X-ray diffraction patterns showed that all the samples are well crystallized and phase pure with a very strong peak and three weak peaks [1,2]. A typical XRD pattern of Al-MCM-41 is shown in Figure 1. It was observed from nitrogen sorption and XRD studies that the samples prepared with aluminum sulfate are less crystalline compared to the

other two series of samples prepared with different aluminum sources. However, the incorporation of aluminum framework was found to be efficient with aluminum isopropoxide and aluminum sulfate, compared to pseudo beohmite. The aluminum incorporation was characterized by increase in the interplanar spacings from XRD and ^{27}Al MAS NMR. The acidity due to the presence of aluminum in the framework was determined by a thermal analysis of n-butylamine on samples. As the aluminum incorporation is higher in samples prepared with aluminum sulfate and aluminum isopropoxide, they have shown better acidity compared to other samples prepared with pseudo boehmite [11].

Catalytic test results in the reactions of hydrogenation of naphthalene and phenanthrene, isopropylation of naphthalene, and hydrocracking of 1,3,5-triisopropylbenzene are presented in Tables 2-5. The initial observation is that they are active in these reactions with good conversions. However, reactions occurred non-selectively as expected, because of the no shape-selective nature of mesoporous materials with wide pores.

In the case of hydrogenation of naphthalene, conversion was almost hundred percent with all the catalysts (see Table 2). There was a large amount of unconverted tetralin observed for the MCM-41 catalysts prepared with pseudo beohmite, whereas for other MCM-41 catalysts the conversion of tetralin to decalin was almost complete. The *t*-decalin/*c*-decalin ratios for all the MCM-41 catalysts are low and in case of the MCM-41 catalyst prepared with pseudo boehmite the ratio is lower compared to the earlier results reported on mordenite [12,13]. These results indicate that in this reaction, the isomerization of *c*-decalin to *t*-decalin probably takes place on acid sites. If that is the case, MCM-41 samples are less acidic as compared to mordenite, hence the *t*-decalin/*c*-decalin ratio is low for these materials. Moreover this ratio is lower for the MCM-41 catalyst prepared with pseudo beohmite because of the poor incorporation of aluminum in the framework, leading to poor acidity.

Table 3 shows the product analyses in hydrogenation of phenanthrene over three different MCM-41 catalysts. They were all active but product selectivities were different compared to earlier results reported [14]; especially sym-octahydroanthracene was formed less, which is an isomerized product from sym-octahydrophenanthrene. This isomerization was believed to be occurring on acid sites [14]. Hence MCM-41 catalysts are not as acidic as other zeolites, especially the MCM-41 catalyst prepared with pseudo beohmite. Similar observations were reported by earlier authors [6,8].

The product analyses of isopropylation of naphthalene using propylene are presented in Table 4. The alkylation over zeolites is known to occur on acid sites. The MCM-41 catalyst prepared with pseudo beohmite was not as active as the other two MCM-41 catalysts. It indicates that the catalyst prepared with pseudo beohmite is less acidic, which again confirms the poor incorporation of aluminum in the framework compared to the other two catalysts. From the product analyses it is also clear that tri and tetra isopropylnaphthalene are formed in large quantities which is a clear indication of non selective nature of these mesoporous materials compared to other zeolites [12, 13]. Non selective nature of these mesoporous materials can also be verified from the α and β substituted product selectivities, which are different from the results obtained on mordenite and Y zeolites [12,13].

Table 3 also shows the effect of Pt loading in the reaction of isopropylation of naphthalene. Both Pt and non Pt containing catalyst showed more or less similar activity, however, selectivities were different. The Pt loaded catalyst yielded more tri and tetra substituted isopropylnaphthalenes, which indicates that the alkylation processes seems to be more efficient with Pt loaded catalysts. This may be due to the bifunctional nature of the catalyst. In zeolite catalysis, it is a known fact that the bifunctional catalysts are more susceptible to the coke formation. In these experiments, because of less reaction time and with limited availability of propylene, deactivation due to coke has not been noticed. However, with continuous supply of propylene for longer reaction times there might be a noticeable difference in catalyst stabilities with and without Pt loading.

In alkylation reactions over zeolites, the type of alkylating agent is known to have an effect. For example, the alkylation with alchols was found to be less efficient compared with respective alkenes [13]. This could be due to the water formation in the reactions with alcohol and water, that may be suppressing the activity of acid sites. Similar results were observed with these mesoporous molecular sieves. The conversion of naphthalene to isopropylnaphthalenes was found to be less when isopropanol was used as an alkylating agent compared to propylene.

Apart from the hydrogenation and alkylation, hydrocracking is an important reaction in the process of upgrading the heavy oils. Zeolites are known to be good hydrocracking catalysts with good activity, selectivity, and stability. Table 5 shows the results of hydrocracking of bulky molecule, 1,3,5 triisopropylbenzene over mesoporous molecular sieves. Both Pt/Al-MCM-41 and H/Al-MCM-41 were found to be active in this reaction. The main products on H/Al-MCM-41 were mono and di substituted isopropylbenzenes. However, the conversion of Pt loaded catalyst is 100% and products were of lower molecular weight, mainly C_3-C_5 hydrocarbons. This may be due to the hydrogenation reaction thus leading to further cracking. The conversion of 1,3,5 triisopropylbenzene was negligible without catalyst at similar conditions.

CONCLUSIONS

We observed that mesoporous molecular sieve catalysts are capable of converting bulky polycyclic aromatic hydrocarbons. Due to the large size of mesopores relative to the substrate molecules, however, reactions are found to be occurring non-selectively. The efficiency of the mesoporous

molecular sieves can be significantly different depending on their synthesis method, especially with the source of aluminum used. The catalysts prepared with aluminum isopropoxide and aluminum sulfate were found to be more active compared to the ones prepared with pseudo boehmite. The Pt loading and type of alkylating agent are influential in the conversion of polycyclic aromatic compounds, as reflected in the product selectivities.

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Figure 1. A typical X-ray powder diffraction pattern of Al-MCM-41 molecular sieves

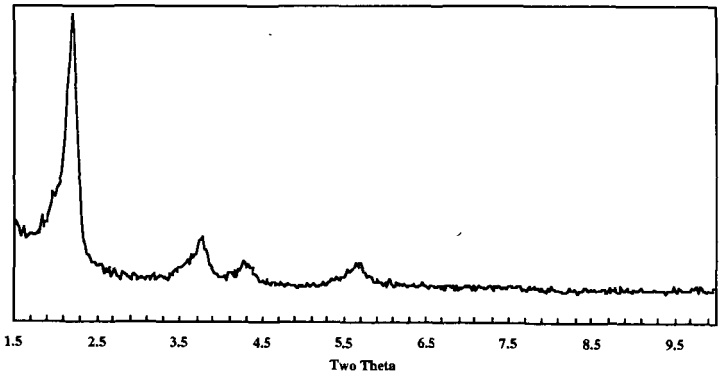

Table 1. Synthesis and physical characteristics of mesoporous molecular sieves

Sample	Source of Al	SiO_2/Al_2O_3 (mole ratio) Input	SiO_2/Al_2O_3 (mole ratio) Output	BET surface Area (m^2/g)	Pore Size from sorption (Å)
MRK9a	Al isopropoxide	100	88.4	1147	27.67
MRK9b	Al isopropoxide	50	53.8	1206	28.02
MRK10a	Catapal B	100	95.5	1010	21.92
MRK10b	Catapal B	50	44.3	----	-----
MRK11a	Al sulfate	100	164.6	834	25.38
MRK11b	Al sulfate	50	87.4	----	-----

Table 2. Naphthalene hydrogenation over Pt/MCM-41 catalysts

Reaction conditions: 0.1 g catalyst, 1.0 g naphthalene, 1000 psi H_2 pressure
200 °C temperature and 1 hour reaction time

Catalyst	naphthalene conv. (%)	Product distribution (wt%)				*t-/c-* decalins
		tetralin	*t*-decalin	*c*-decalin	total decalins	
MRK9b	100.0	0.18	33.15	66.67	99.82	0.497
MRK10b	99.7	25.50	18.01	56.48	74.49	0.319
MRK11b	100.0	0.00	32.25	67.75	100.00	0.476

Table 3. Hydrogenation of phenanthrene over Pt/MCM-41 catalysts

Reaction conditions: 0.1 g catalyst, 1.0 g phenanthrene, 1500 psi H_2 pressure
300 °C temperature and 2 hours reaction time

	Product distribution (wt%)		
	MRK9b	MRK10b	MRK11b
Phenanthrene Conv. (%)	79.61	88.00	66.63
1,2,3,4-tetrahydrophenanthrene (THP)	7.03	6.84	14.69
9,10-dihydrophenanthrene (DHP)	41.59	45.47	54.29
sym-octahydrophenanthrene (sym-OHP)	14.82	31.25	13.25
sym-octahydroanthracene (sym-OHA)	16.70	1.40	7.71
unsym-octahydrophenanthrene (unsym-OHP)	15.27	12.99	9.51
tetradecahydrophenanthrenes (TDHP)	3.94	2.03	0.00
sym-OHA/sym-OHP	1.41	0.07	0.09

Table 4. Isopropylation of naphthalene over MCM-41 catalysts

Reaction conditions: 0.1 g catalyst, 1.0 g naphthalene, 150 psi propylene
200 °C temperature and 2 hours reaction time

Catalyst	Product distribution (wt%)			
	H/MRK9b	Pt/MRK9b	Pt/MRK10b	Pt/MRK11b
naphthalene Conv. (%)	92.48	96.62	37.41	90.25
2-isopropylnaphthalene	11.82	9.13	24.59	11.57
1-isopropylnaphthalene	16.27	9.88	56.13	20.24
diisopropylnaphthalenes	42.11	39.25	16.41	42.19
triisopropylnaphthalenes	25.37	34.26	2.51	22.35
tetraisopropylnaphthalens	4.41	7.46	0.29	3.63
2,6-diisopropylnaphthalenes	3.18	4.87	0.80	2.09
2,7 di isopropyl naphthalenes	3.96	3.83	0.77	2.09

Table 5. Hydrocracking of 1,3,5-triisopropylbenzene over MCM-41 catalysts

Reaction conditions: 0.1 g catalyst, 1.0 g triisopropylbenzene, 1500 psi H_2 pressure
350 °C temperature and 2 hours reaction time

Catalyst	Product distribution (wt%)		
	no catalyst	H/MRK9b	Pt/MRK9b
1,3,5-triisopropylbenzene Conv. (%)	1.02	67.69	100.0
isopropylbenzene	0.00	19.56	0.0
1,3-diisopropylbenzene	94.20	63.09	0.0
1,4-diisopropylbenzene	3.30	7.71	0.0
others, mainly C_3-C_5 hydrocarbons	4.10	9.63	100.0